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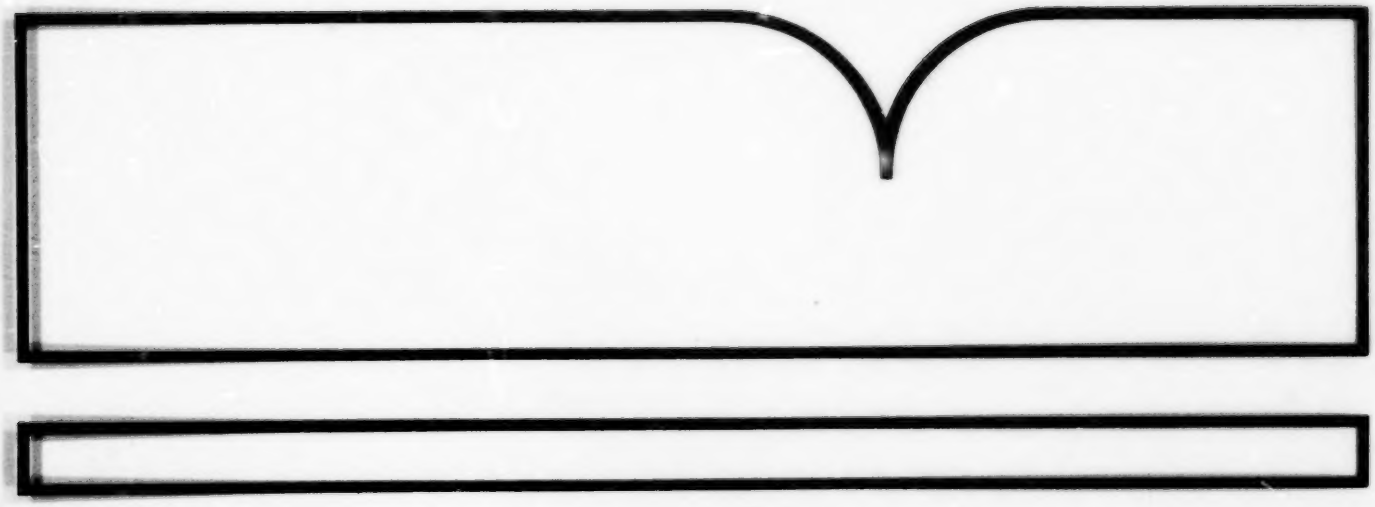

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JUNE-SEPTEMBER, 6-9 AM, AMBIENT AIR BENZENE CONCENTRATIONS IN 39 U.S. CITIES, 1984-1986

by

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16. ABSTRACT

Ambient air samples from 44 sites in 39 U.S. urban areas were collected in electropolished, stainless steel canisters on week days from 6 to 9 am during June through September of 1984, 1985, and 1986. Not all sites were sampled all years. Samples were analyzed by capillary gas chromatography with flame ionization detection to determine C_2 to C_{12} volatile hydrocarbon composition. Benzene, which is carcinogenic and present in automobile exhaust and gasoline, was present in every sample. Individual sample concentrations ranged from 1.0 parts-per-billion as carbon (ppbC) to 273 ppbC. The benzene median concentrations by site and year ranged from 4.8 ppbC to 35.0 ppbC with the overall median being 12.6 ppbC.

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JUNE-SEPTEMBER, 6-9 AM, AMBIENT AIR BENZENE CONCENTRATIONS IN 39 U.S. CITIES, 1984-1986

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Ambient air samples from 44 sites in 39 U.S. urban areas were collected in electropolished, stainless steel canisters on week days from 6 to 9 am during June through September of 1984, 1985, and 1986. Not all sites were sampled all years. Samples were analyzed by capillary gas chromatography with flame ionization detection to determine C2 to C12 volatile hydrocarbon composition. Benzene, which is carcinogenic and present in automobile exhaust and gasoline, was present in every sample. Individual sample concentrations ranged from 1.0 parts-per-billion as carbon (ppbC) to 273 ppbC. The benzene median concentrations by site and year ranged from 4.8 ppbC to 35.0 ppbC with the overall median being 12.6 ppbC.

Introduction

Benzene is a known human and animal carcinogen (1) which has been designated as a hazardous air pollutant under Section 112 of the Clean Air Act (2). Benzene is present in gasoline and the emissions from gasoline fueled vehicles. Levels in gasoline range from 0 to 4% by volume with a national average of 1.3% (3). The major source of benzene in ambient air is mobile sources. In 1982, for example, mobile sources contributed 85% of benzene emissions. Of this 85%, 82% was due to exhaust emissions, 17% from evaporative emissions, and 1% from refueling operations. Gasoline-powered vehicles accounted for 95% of mobile source benzene (4). Stationary sources of benzene include fugitive emissions, coke by-products, chemical production, gasoline marketing, benzene storage, and solvent use. Benzene is ubiquitous in ambient air. Data on ambient air concentrations of benzene and other hazardous organic chemicals were assembled by Brodzinsdy and Singh from 241 references covering primarily the years 1970 through 1980 (5). They reported a median concentration of 2.8 ppb by volume derived from 2292 measurements in urban/suburban areas of the U.S. Even with this large number of measurements, they were unable to perform trend analysis, because most concentrations were day-time measurements made during the warmer half of the year.

EPA initiated a multi-year project in 1984 to obtain 6-9 am total non-methane organic compound (NMOC) concentrations from selected U.S. cities. Between 10 and 15% of the samples were analyzed to determine speciated hydrocarbon compositions. Benzene was one of the hydrocarbons determined. Over the project's three years more than 900 samples were analyzed.

Experimental Methods

Ambient air was sampled daily from 6 to 9 am from June through September each year. Samples were pumped into evacuated, electropolished, stainless steel (ss) spheres and air freighted back to Research Triangle Park for analysis. The sampling protocol and equipment are described in detail elsewhere (6,7).

Benzene was determined on a Hewlett-Packard model 5880A gas chromatograph (gc) equipped with a flame ionization detector (fid) and outfitted with a dual valve cryogenic preconcentration system designed to condense 470-ml of air for injection onto a gc column. C_2 to C_{12} hydrocarbons including benzene were condensed in an 18-cm by 3.2-mm o.d. ss trap containing 60-80 mesh glass beads at liquid oxygen temperature (-183° C) and separated on a 60-m, 0.32-mm i.d. fused silica column with a 1.0-um thick film of DB-1 bonded liquid phase. The column temperature program was -50° C for 1 min to 200° C at 8°/min. The fid was operated at 270° C. An IBM PC-XT with 640K RAM was used to receive and process the gc data. A National Bureau of Standards propane-in-air standard reference material was used for calibration of all hydrocarbons. The benzene limits of detection and quantification were estimated to be 0.04 and 0.12 parts-per-billion as carbon (ppbC) respectively. Benzene and other hydrocarbons were identified by retention time.

Results and Discussion

Table I is a statistical summary showing the number of samples, median, minimum, and maximum benzene concentration in ppbC by year for each site. During the three years of the study samples were analyzed from 44 sites in 39 cities. The five cities with two sites are shown with a "-1" or "-2" after the city in the table. Four of the Texas cities, Philadelphia, and Washington, DC were sampled all three years. The other four Texas cities, Atlanta, Birmingham, Kansas City, and Richmond were sampled during two of the three years. The remaining 25 cities were sampled only one year. The total number of analyses for all cities over all years was 812, although the number per city ranged widely from only three at Miami to 50 at Dallas.

The individual sample benzene concentrations ranged from a low of 1.0 ppbC at Orange in 1984 to 273 ppbC at Birmingham in 1986. The median concentrations ranged from 4.8 ppbC at West Palm Beach to 35.0 ppbC at Memphis, with an overall median of 12.6 ppbC for all sites. For 1984 and 1985, the median percent benzene fraction of NMOC ranged from 1.2 to 3.1 with an average of 1.9. The variation of benzene relative to NMOC was much less than the variation of the absolute or median concentrations. This suggests that benzene concentrations are highly correlated with total NMOC, which is consistent with the high percentage mobile source contribution to ambient air benzene concentrations. A high mobile source contribution to NMOC levels in urban areas is expected during the 6 to 9 am period.

The contribution of benzene from mobile sources can be estimated by multiplying measured ambient air acetylene concentrations by the benzene:acetylene ratio determined from a high mobile source area such as a tunnel (8). We calculated the vehicular benzene contribution for all of the 1984 and 1985 samples using the benzene:acetylene ratio (0.92) that we had determined for the Lincoln Tunnel in 1982. The results indicated that mobile source emissions contributed at least 90% of the benzene present in 92% of the 1984 and 1985 samples. The cities that showed significant evidence of sources other than mobile were St. Louis and Indianapolis in addition to four Texas cities, Beaumont, Clute, Orange, and Texas City. Texas City was the most prominant with 36% of its samples indicating at least a 10% contribution by stationary sources.

Conclusions

Ambient air benzene concentrations for 6 to 9 am in the 39 U.S. cities reported here were quite low. The site median concentrations ranged from 4.8 to 35.0 ppbC and the overall median was 12 ppbc. The data also indicated that mobile sources were the major source of benzene in the vast majority of samples.

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Table I. Statistical summary of benzene concentrations.

City	Year	N	Concentration, ppbC Median	Min	Max
Akron OH	1984	10	6.0	4.6	15.2
Atlanta GA	1984	7	9.6	3.7	53.5
Atlanta GA	1986	14	11.2	4.0	27.8
Baltimore MD	1986	7	16.9	8.2	30.9
Baton Rouge LA	1985	16	8.3	2.4	23.5
Beaumont TX	1984	9	10.7	5.2	33.1
Beaumont TX	1985	19	14.1	6.8	49.4
Beaumont TX	1986	13	11.3	6.2	36.9
Birmingham AL	1984	6	8.4	7.8	185.7
Birmingham AL	1986	13	18.7	6.3	273.2
Boston MA	1985	8	6.0	3.9	15.9
Bridgeport CT	1986	16	8.9	3.5	33.4
Brooklyn NY	1986	16	13.7	5.0	38.5
Charlotte NC	1984	16	6.9	2.6	25.4
Chattanooga TN	1984	12	22.0	8.4	65.4
Chicago-1 IL	1986	8	27.3	14.1	48.4
Chicago-2 IL	1986	14	20.7	3.8	30.3
Cincinnatti OH	1984	7	10.4	6.4	22.5
Cleveland OH	1985	17	23.7	5.2	60.9
Clute TX	1984	10	9.4	3.9	26.9
Clute TX	1985	17	12.0	1.3	34.8
Dallas TX	1984	13	10.0	4.5	24.4
Dallas TX	1985	23	12.6	5.7	34.9
Dallas TX	1986	14	11.5	4.2	21.3
Denver-1 CO	1986	12	16.7	6.3	39.6
Denver-2 CO	1986	13	24.5	17.9	39.5
El Paso TX	1984	8	18.8	6.0	39.2
El Paso TX	1985	17	16.0	6.3	39.4
El Paso TX	1986	9	20.0	6.9	41.6
Fort Worth TX	1984	13	14.2	8.6	37.4
Fort Worth TX	1985	19	13.0	5.8	26.0
Fort Worth TX	1986	16	10.5	6.2	40.4

Table I continued

City	Year	N	Median	Min	Max
Houston-1 TX	1985	22	16.1	5.2	50.9
Houston-1 TX	1986	14	22.5	7.5	112.3
Houston-2 TX	1986	12	22.7	10.9	31.7
Indianapolis IN	1984	10	18.9	9.1	76.2
Kansas City MO	1984	11	12.4	5.8	34.8
Kansas City MO	1985	18	9.7	4.1	22.6
Lake Charles LA	1985	16	11.9	3.8	18.2
Manhattan NY	1986	12	10.5	5.3	31.8
Memphis TN	1984	8	35.0	17.8	47.0
Miami FL	1984	3	12.9	7.6	17.3
New Haven CT	1986	16	10.5	2.6	57.5
Orange TX	1984	10	8.5	1.0	14.5
Orange TX	1985	16	7.8	1.8	46.4
Philadelphia-1 PA	1984	7	15.2	8.5	27.8
Philadelphia-1 PA	1985	13	15.6	6.3	31.0
Philadelphia-1 PA	1986	14	6.0	1.9	17.9
Philadelphia-2 PA	1985	11	19.6	6.9	51.0
Portland ME	1985	13	10.4	2.4	18.1
Richmond VA	1984	10	6.4	2.6	10.0
Richmond VA	1985	14	9.8	4.7	18.5
Salt Lake City-1 UT	1986	14	21.4	8.8	41.8
Salt Lake City-2 UT	1986	13	26.1	9.7	47.2
Scranton PA	1984	9	7.1	3.2	18.5
St Louis MO	1985	18	11.1	3.8	72.7
Texas City TX	1984	13	12.0	5.5	47.3
Texas City TX	1985	15	12.6	3.4	119.4
Trenton NJ	1986	16	13.1	8.0	36.6
Tulsa OK	1986	12	7.7	2.6	65.2
Washington DC	1984	10	17.8	13.8	33.5
Washington DC	1985	11	15.3	7.3	23.5
Washington DC	1986	11	5.6	3.7	25.3
West Palm Beach FL	1984	8	4.8	2.6	9.7